

## OHM REMEDIATION SERVICES CORPORATION (Oxygen Microbubble In Situ Bioremediation)

### TECHNOLOGY DESCRIPTION:

The use of in situ bioremediation on contaminated soils and groundwater is becoming more widespread and accepted; however, one of the difficulties with in situ bioremediation is the limitations of oxygen delivery to the microflora for the degradation of the target contaminant. Oxygen microbubble technology may be effective in overcoming this limitation.

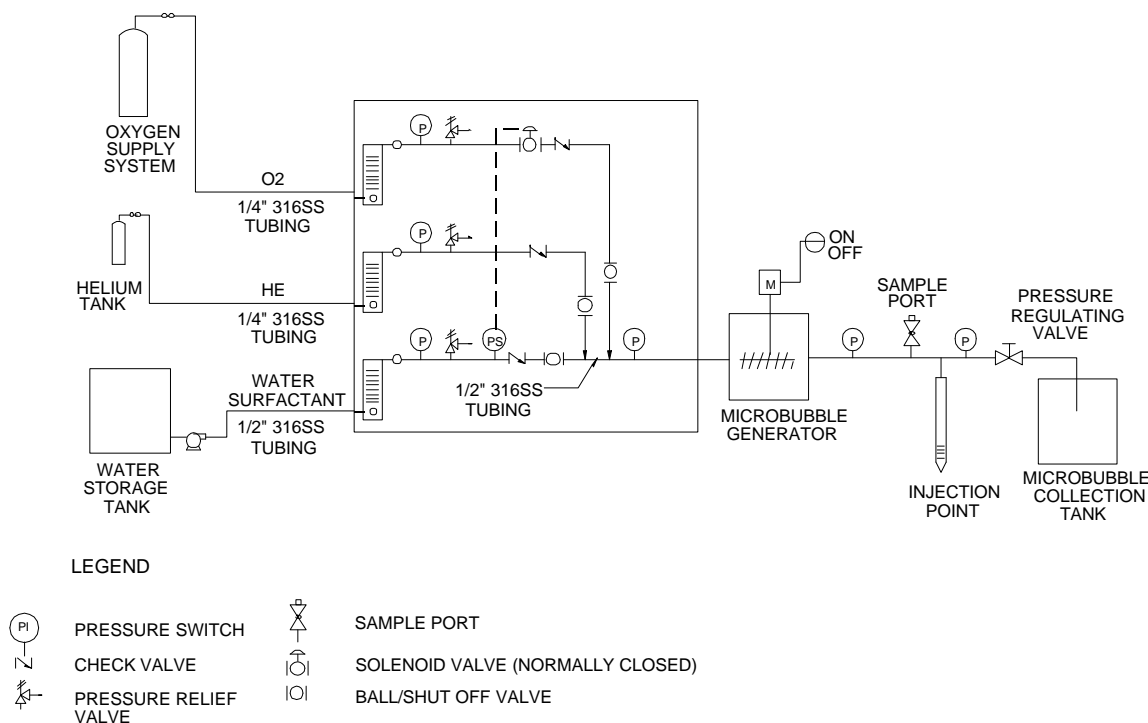
The oxygen microbubble technology (see figure below) uses a continuously generated stream of oxygen and water solution containing low concentrations of a surfactant. A water stream containing about 200 milligrams per liter of surfactant is mixed with oxygen under pressure. The resulting oxygen and water mixture is pumped through a microbubble generator that produces a

zone of high-energy mixing. The result is a 60 to 80 percent by volume dispersion of bubbles with a typical bubble diameter ranging from 50 to 100 microns. The microbubble dispersion is then pumped through an injection well into the treatment zone. The microbubbles deliver oxygen into the contaminated groundwater, providing an oxygen source for the biodegradation of the contaminant by the indigenous microflora.

### WASTE APPLICABILITY:

The process has successfully treated groundwater contaminated with a number of organic compounds including volatile organic compounds, semivolatile organic compounds, and petroleum hydrocarbons.

### STATUS:



Oxygen Microbubble In Situ Bioremediation of Groundwater

The Oxygen Microbubble In Situ Bioremediation process was accepted into the Emerging Technology Program in summer 1992. This process is being evaluated at a jet fuel spill site at Tyndall Air Force Base in Panama City, Florida.

The overall objective of this project is to evaluate the in situ application of the oxygen microbubble technology for bioremediation. The goals are to determine the subsurface oxygen transfer to the groundwater, retention of the microbubble in the soil matrix, and the biodegradation of the petroleum hydrocarbons present in the soil and groundwater.

A pilot test was performed at the site in 1995. The objective of this test was to determine the rate at which generated microbubbles could be injected into the surficial aquifer at the site. In addition, changes that occurred in the microbubbles and the aquifer during injection were monitored. Parameters that were monitored included the following:

- Microbubble quality, quantity, and stability
- Microbubble injection rate and pressure
- Lateral migration rates of microbubbles
- Lateral extent of migration of surfactant in the aquifer
- Lateral changes in dissolved oxygen concentration in the aquifer
- Rate of migration of tracer gas (helium) in the vadose zone
- Oxygen in the vadose zone

The pilot test verified that microbubbles can be injected into a shallow aquifer consisting of unconsolidated, fine-grained sediments. The study also verified that aquifer characteristics allowed the injection of the microbubble foam at rates of at least 1 gallon per minute (foam). Continued injection of foam after about 45 minutes resulted in coalescence of the foam based on pressure measurements. The microbubble foam was observed to be persistent in the aquifer for long periods of time. This testing supported the use of oxygen microbubbles as an oxygen delivery system for in situ bioremediation.

The next testing phase at the site began in fall 1996. During this test, multiple injection points will be used to determine the maximum rate of foam

injection while maintaining foam stability. Oxygen will be used as the gas for microbubble production. The retention of oxygen microbubbles will be compared to sparged air to determine oxygen delivery efficiency.

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**PHYTOKINETICS, INC.**  
**(Phytoremediation of Contaminated Soils)**

**TECHNOLOGY DESCRIPTION:**

Phytoremediation is the use of plants for the in situ cleanup of contaminated soils, sediments, and water. The specific technology described in this profile is the use of grasses to remediate surface soils contaminated with organic chemical wastes. Many types of organic contaminants, including pentachlorophenol (PCP), biodegrade more rapidly in planted soils than in unplanted soils.

The ability of plants to enhance biodegradation is based, in part, on plant root exudates. Plants release into the soil organic chemical exudates (sugars, acids, alcohols, and proteins) which can enhance biodegradation in the following ways: (1) the exudates stimulate soil microorganisms in the rhizosphere (the zone immediately surrounding the plant root) by serving as a food source. Rhizosphere soils contain 10 to 100 times more metabolically active microorganisms than unplanted soils; (2) exudates from the roots contain enzymes

which can transform organic contaminants; (3) exudates can stimulate cometabolic transformations of contaminants by soil microorganisms.

Another important factor in phytoremediation is that plants themselves can take up and detoxify certain organic contaminants. Also, plants can stabilize soils against erosion by wind and water. Grasses appear to be ideal for phytoremediation of surface soils because their fibrous root systems form a continuous dense rhizosphere.

**WASTE APPLICABILITY:**

Organic chemical contaminants which are more rapidly removed in planted (rhizosphere) soils than unplanted soils include PCP, certain polycyclic aromatic hydrocarbons (PAH), chlorinated solvents, insecticides, and nitroaromatic explosives. For phytoremediation to be effective, soil contaminants must be in the surficial soil, within the root zone of plants (top 2 to 3 feet), and must be present at



Greenhouse-Scale Phytoremediation Study



Small-Scale Outdoor Study

intermediate, non-phytotoxic levels. Although phytoremediation may be cost effective, especially for larger sites, it is slower than more intensive approaches (such as excavation or ex situ treatments) and may require several growing seasons.

## **STATUS:**

This technology was accepted into the Emerging Technology Program in 1995 for a 2-year greenhouse and field trial. Under the Emerging Technology Program, Phytokinetics, Inc. (Phytokinetics), will demonstrate the effectiveness of the technology for surficial soils contaminated with PCP and PAHs from the McCormick & Baxter (M&B) Superfund site in Portland, Oregon. The plant species used is perennial ryegrass (*Lolium perenne*).

The study consists of two phases. The first phase, which began in March 1996, consists of a greenhouse study conducted under optimal conditions for plant growth. The second phase, which began in April 1996, is taking place in the field, at an area within the M&B site (see photographs on previous page). For both phases, contaminant removal rates are being compared in planted and unplanted (nutriated) soils, as well as in unplanted unamended soils. The latter treatment allows assessment of rates of natural (intrinsic) bioremediation. Preliminary results from the first phase suggest that plants accelerate initial rates of removal of PCP, chrysene, benzo(a)anthracene, and pyrene relative to controls.

Phytokinetics' personnel have also conducted laboratory-scale studies using crested wheatgrass (*Agropyron cristatum*). The fate of uniformly radiolabeled PCP, added to soil at a concentration of 100 milligrams per kilogram (mg/kg), was compared in three planted and three unplanted systems. Employing a specifically designed flow-through test system, a budget was maintained for the PCP-derived radiolabel, and the extent of mineralization and volatilization of the radiolabel were monitored during a 155-day test.

In the unplanted systems, an average of 88 percent of the total radiolabel remained in the soil, and only 6 percent was mineralized. In the planted systems,

33 percent of the radiolabel remained in the soil, 22 percent was mineralized, and 36 percent was associated with plant tissue. Other tests using the same system were conducted with radiolabeled pyrene (initial concentrations of 100 mg/kg soil). The onset of mineralization occurred sooner in planted systems (mean = 45 days) than in unplanted systems (mean = 75 days). However, the extent of radiolabeled pyrene mineralization was the same in the two types of systems.

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## PINTAIL SYSTEMS, INC. (Biomineralization of Metals)

### TECHNOLOGY DESCRIPTION:

Pintail Systems, Inc. (PSI), has evaluated the use of bioremediation processes for in situ biomineralization of heavy metals in mine wastes. Biomineralization processes are part of a natural cycle in which minerals are continuously formed, transformed, and degraded. In situ biomineralization capitalizes on the role that microorganisms play in natural ore formation and involves accelerating the biological reactions to remediate waste.

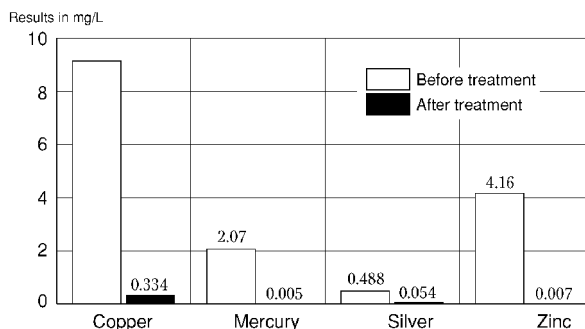
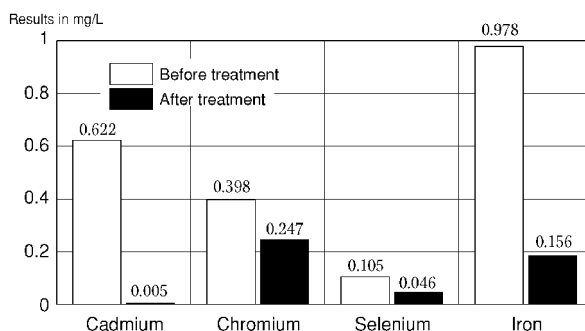
During biomineralization, microorganisms initiate a complex series of reactions. Effective metal removal mechanisms are influenced by biologically catalyzed

remineralization reactions. PSI's research indicates that biomineralization begins when microorganisms attach to the ore's surface, forming a "bioslime" layer. Soluble metals then bind to cell walls and extracellular products. Next, metal hydroxides, oxides, and carbonates precipitate into the bioslime layer as amorphous mineral precursors, which provide a template for further mineralization as they stabilize.

A microbial population for biomineralization may be used in either batch or continuous treatment mode for in situ bioremediation. In batch mode, bacteria and nutrient solutions may be applied directly to contaminated soil, sediments, or aqueous solutions to catalyze bioaccumulation and

### 2.5 million ton Spent Ore Cyanide Field Detox

Metals analysis before and after application of bacteria treatment solutions to the heap to degrade cyanide. Analysis of heap leachate solutions.



### Biomineralization of Metals

biomineralization. For continuous treatment, microorganisms may be immobilized in a porous matrix or fixed film reactor to remove metals from aqueous solutions.

### **WASTE APPLICABILITY:**

The PSI biomineralization process is designed to treat solids (soils, sludges, and sediments) that contain heavy metals or organics. It can also be applied to acid rock drainage that occurs naturally or results from mining or energy production operations. The process can be applied at battery waste sites, urban lead sites, mines, and metal production and fabrication sites.

### **STATUS:**

This technology was accepted into the Emerging Technology Program in 1995. Under the Emerging Technology Program, PSI intends to complete development of its biomineralization process, resulting in a field-ready in situ biomineralization technology. PSI will conduct batch and continuous treatment tests at its laboratory and pilot plant in Aurora, Colorado, using soils, ore, sludges, and tailings from several Superfund sites.

PSI has developed and applied full-scale detoxification processes for spent ore at several mines in the western U.S. In addition to cyanide detoxification, metals removal or remineralization has been observed during treatment at these mines. PSI has also demonstrated biomineralization of metals in laboratory- and pilot-scale tests for mining industry clients at mines in Idaho, Nevada, Arizona, California, Colorado, Mexico, and Canada, including the Summitville Mine Superfund site in Colorado. Results from the use of biomineralization is shown in the figure on the previous page.

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## **PULSE SCIENCES, INC.**

### **(X-Ray Treatment of Organically Contaminated Soils)**

#### **TECHNOLOGY DESCRIPTION:**

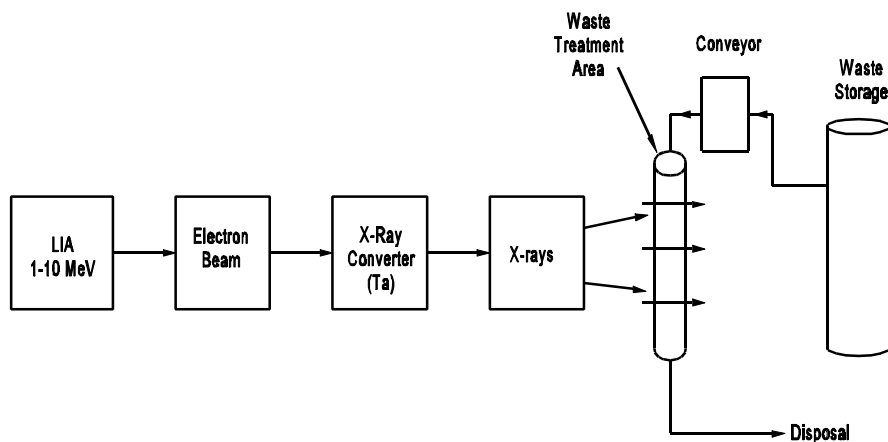
X-ray treatment of organically contaminated soils is based on in-depth deposition of ionizing radiation. Energetic photons (X-rays) collide with matter to generate a shower of lower-energy, secondary electrons within the contaminated waste material. These secondary electrons ionize and excite the atomic electrons, break up the complex contaminant molecules, and form highly reactive radicals. These radicals react with contaminants to form compounds such as water, carbon dioxide, and oxygen.

Other sources of ionizing radiation, such as ultraviolet radiation or direct electron beam processing, do not penetrate the treatable material deeply enough. Ultraviolet radiation heats only the surface layer, while a 1.5-million electron volt (MeV) electron penetrates about 4 millimeters into the soil. X-rays, however, penetrate up to 20 centimeters, allowing treatment of thicker samples. In situ treatment, which reduces material handling requirements, may also be possible with X-ray treatment.

An efficient, high-power, high-energy, linear

induction accelerator (LIA) plus X-ray converter generates the X-rays used in the treatment process (see figure below). The LIA energy, which must be small enough to avoid nuclear activation and as large as possible to increase the bremsstrahlung conversation efficiency, usually ranges from 8 to 10 MeV. A repetitive pulse of electrons 50 to 100 nanoseconds long is directed onto a cooled converter of high atomic number to efficiently generate X-rays. The X-rays penetrate and treat the organically contaminated soils.

The physical mechanism by which volatile organic compounds (VOC) and semivolatile organic compounds (SVOC) are removed primarily depends on the contaminant present. Because of the moisture in contaminated soil, sludge, and sediments, the shower of secondary electrons resulting from X-ray deposition produces both highly oxidizing hydroxyl radicals and highly reducing aqueous electrons. While hazardous by-products may form during X-ray treatment, contaminants and by-products, if found, may be completely converted at sufficiently high dose levels without undesirable waste residuals or air pollution.



X-Ray Treatment Process

X-rays can treat contaminated soil on a conveyor or contained in disposal barrels. Since X-rays penetrate about 20 centimeters into soil, large soil volumes can be treated without losing a significant fraction of the ionizing radiation in standard container walls. Pulse Sciences, Inc., estimates that the cost of high throughput X-ray processing is competitive with alternative processes which decompose the contaminants.

### **WASTE APPLICABILITY:**

X-ray treatment of organically contaminated soils has the potential to treat large numbers of contaminants with minimum waste handling or preparation. Also, X-ray treatment can be applied in situ. In situ treatment may be of significant importance in cases where it is impossible or impractical to reconfigure the waste volume for the ionizing radiation range of electrons or ultraviolet radiation. Treatable organic contaminants include benzene, toluene, xylene, trichloroethene, tetrachloroethene, carbon tetrachloride, chloroform, and polychlorinated biphenyls.

### **STATUS:**

This technology was accepted into the SITE Emerging Technology Program in 1993. A 1.2-MeV, 800-ampere (amp), 50-watt LIA and a 10.8-MeV, 0.2-amp, 10,000-watt radio frequency (RF) linac will be used in the program. The primary objectives are to (1) demonstrate that X-ray treatment can reduce VOC and SVOC levels in soils to acceptable levels, and (2) determine any hazardous by-product that may be produced.

Samples with identical initial contaminant concentration levels will be irradiated at increasing dose levels to determine (1) the rate (concentration versus dose) at which the contaminants are being destroyed, and (2) the X-ray dose required to reduce organic contamination to acceptable levels. The 10.8-MeV RF linac, which produces more penetrating X-rays, should provide information on the optimum X-ray energy for the treatment process. Increasing the accelerator energy allows a more efficient conversion from electrons to X-rays in the converter, but an upper limit (about 10 MeV) restricts the energy treatment, since higher energy activates the soil. The experimental database will be used to develop a conceptual design and cost estimate for a high throughput X-ray treatment system.

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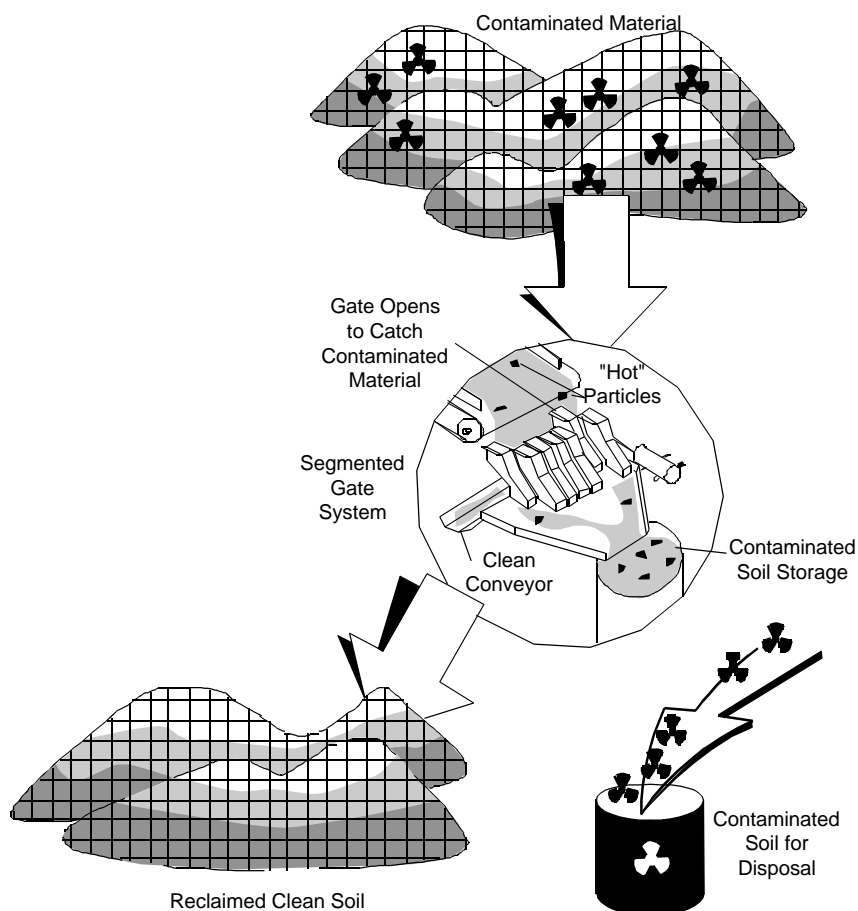
**THERMO NUTECH**  
(formerly TMA THERMO ANALYTICAL, INC.)  
(Segmented Gate System)

**TECHNOLOGY DESCRIPTION:**

TMA Thermo Analytical, Inc. (TMA), has conducted many radiological surveys of soil contaminated with low and intermediate levels of radioactivity. Cleanup of these sites is a highly labor-intensive process requiring numerous personnel to conduct radiological surveys with portable hand-held instruments. When contamination is encountered, an attempt is made to manually excise it. When surveys disclose larger areas of contamination, heavy equipment is used to remove the contaminated material. Since pinpoint excision with earthmoving equipment is difficult, large amounts of uncontaminated soil are removed

along with the contaminant. Few sites have been characterized to be uniformly and/or homogeneously contaminated above release criteria over the entire site area.

As a result, TMA developed the Segmented Gate System (SGS) to physically separate and segregate radioactive material from otherwise "clean" soil (see figure below). The SGS removes only a minimal amount of clean soil with the radioactive particles, significantly reducing the overall amount of material requiring disposal. The SGS works by conveying radiologically contaminated feed material on moving conveyor belts under an array of sensitive, rapidly reacting radiation detectors. The moving material is



TMA's Segmented Gate System

assayed, and radioactivity content is logged. Copyrighted computer software tracks the radioactive material as it is transported by the conveyor and triggers a diversion by one or more of the SGS chutes when the material reaches the end of the conveyor. Clean soil goes in one direction, and contaminated material in another.

The key advantage to this system is automation, which affords a much higher degree of accuracy compared to manual methods. Contaminants can be isolated and removed by locating small particles of radioactive material dispersed throughout the soil. All of the soil is analyzed continuously during processing to document the level of radioactivity in the waste and to demonstrate that cleaned soil meets release criteria. This automation and analysis results in a significant cost reduction for special handling, packaging, and disposal of the site's radioactive waste.

#### **WASTE APPLICABILITY:**

The SGS locates, analyzes, and removes gamma ray-emitting radionuclides from soil, sand, dry sludge, or any host matrix that can be transported by conveyor belts. The SGS can identify hot particles, which are assayed in units of picoCuries, and can quantify distributed radioactivity, which is assayed in units of picoCuries per gram (pCi/g) of host material. The lower limit of detection (LLD) for the system depends on the ambient radiation background, conveyor belt speed, thickness of host material on conveyor, and contaminant gamma ray energy and abundance. However, LLDs for americium-241 of 2 pCi/g and for radium-226 of 5 pCi/g have been successfully demonstrated.

#### **STATUS:**

This technology was accepted into the SITE Emerging Technology Program in July 1994. Pilot- and field-scale tests using TMA-owned mobile equipment were initiated at a U.S. Department of Energy facility in March 1995. Further evaluations have been temporarily postponed. Future tests will demonstrate the technology's applicability to other radionuclides and other host matrices.

A similar system has been used on Johnston Atoll in the mid-Pacific since January 1992; TMA is currently under contract to the U.S. Defense Nuclear Agency to process coral soil contaminated with plutonium and americium using the SGS.

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## UNIVERSITY OF HOUSTON (Concentrated Chloride Extraction and Recovery of Lead)

### TECHNOLOGY DESCRIPTION:

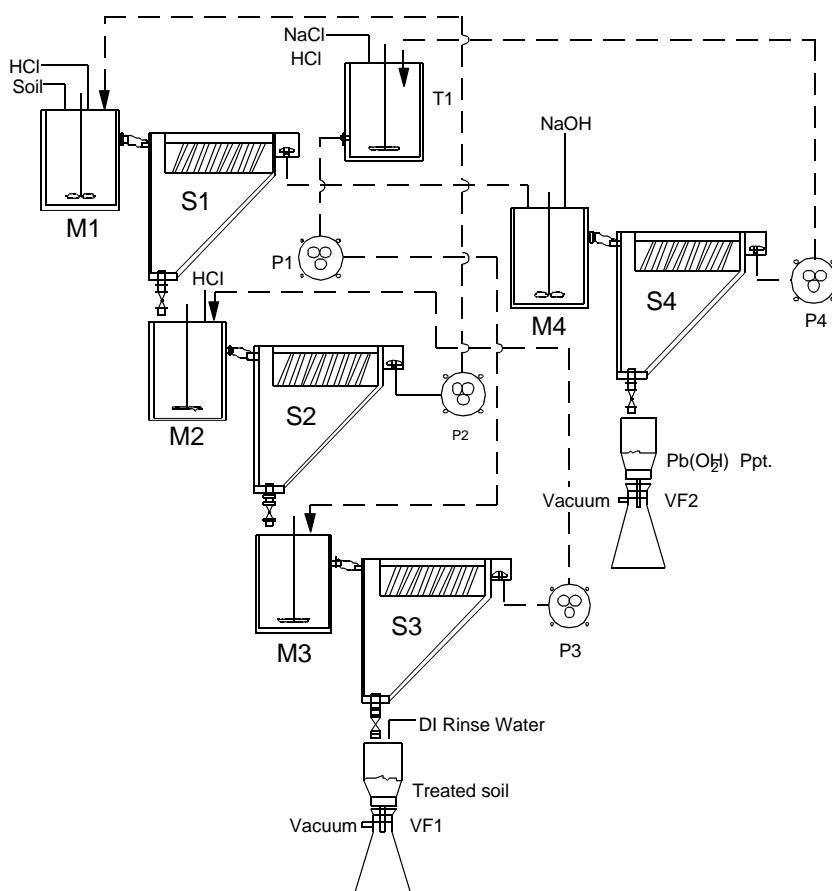
This technology recovers lead from soils using an aqueous solvent extraction process that takes advantage of the high solubility of chlorocomplexes of lead. The extract solution contains greater than 4 molar sodium chloride and operates at a pH of -4. The figure below depicts the three-stage continuous countercurrent pilot plant used to study the process.

To operate the pilot plant, soil is sieved to remove particles greater than 1.12 millimeters in diameter, and is placed in the first chloride extraction tank (M1) for extraction with concentrated chloride solution. This soil and solvent slurry passes into a thickener (S1). The soil and solvent slurry has an

average residence time of 1 hour in each extraction tank in the system.

The bottoms of the thickener flow by gravity to the second chloride extraction tank (M2). The solution exiting the second chloride extraction tank flows to the second thickener (S2). The bottoms of the second thickener feed the third stage.

The third stage is the last soil stage, but the first solvent stage; fresh solvent enters the system at stage three. The bottoms of the third thickener (S3) flow by gravity into the soil rinse system (VF1) to remove excess salt. The rinsed soil in VF1 is the clean product soil. The overflows from S3 pass to M2, the overflows from S2 pass to the M1, and the



Concentrated Chloride Extraction and Recovery  
of Lead (Bench-Scale Process)

overflows from S1 pass to the lead precipitation system (M4/S4). In M4/S4, lead hydroxide  $[\text{Pb}(\text{OH})_2]$  is recovered by simply raising the pH of the spent extraction solution to 10. After  $\text{Pb}(\text{OH})_2$  removal, the spent chloride solution flows to the solvent makeup unit (T1) where it is acidified to pH 4 in preparation for reuse.

This technology produces treated soil, suitable for replacement on site, and  $\text{Pb}(\text{OH})_2$ , possibly suitable for reprocessing to recover pure lead. The ease of solvent regeneration minimizes waste disposal. Solvent recycling is very successful, and pilot-plant tests have required little or no salt or water makeup.

The pilot plant has treated soil from two lead battery waste sites (LBWS). One LBWS soil contained high fines (about 50 percent clay and silt) and the other contained low fines (less than 20 percent clay and silt). The pilot plant's method of transferring soil by gravity eases much of the soil handling problems inherent in high clay soils. After treatment, both soils easily passed the toxicity characteristic leaching procedure test. The total lead concentration in the high fines and low fines soil was reduced from 7 percent to about 0.15 percent and 1.5 percent to 0.07 percent, respectively.

### **WASTE APPLICABILITY:**

This technology removes high concentrations of lead from soil, particularly at LBWS, while producing a treated soil usable as backfill and a recyclable, concentrated lead salt.

### **STATUS:**

This technology was accepted into the SITE Emerging Technology Program in September 1994. Batch extraction testing was completed in 1995. Treatability tests using the pilot plant on the high and low fines soils were completed in August 1996. The high fines soil came from a LBWS located in Houston, Texas, and the low fines soil came from the Sapp Battery National Priority List site in Florida. Future plans include expanding the applications of the technology by studying additional waste-site soils. The evaluation of the technology is expected to be completed by August 1997.

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## UNIVERSITY OF WISCONSIN-MADISON (Photoelectrocatalytic Degradation and Removal)

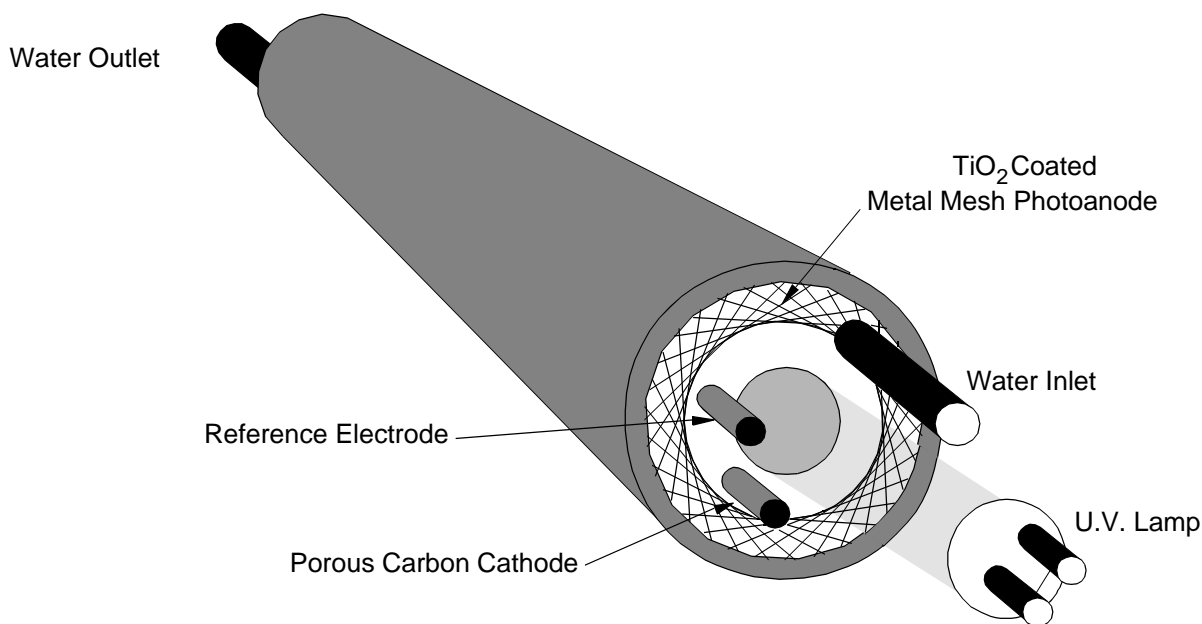
### TECHNOLOGY DESCRIPTION:

The University of Wisconsin-Madison (UW-Madison) is developing a photocatalytic technology that uses titanium dioxide ( $\text{TiO}_2$ ) suspensions to coat various supporting materials used in treatment applications. For this application, the suspensions are used to coat a conductive metallic or carbon mesh. Coating the mesh with a suitable thickness of  $\text{TiO}_2$  catalyst provides the basis for a photoreactor that uses most of the available ultraviolet (UV) radiation. An electrical field can also be applied across the catalyst to improve its performance.

The figure below shows a possible photoreactor design that uses a ceramic film. In this design, the  $\text{TiO}_2$  coating on the porous metal acts as a photoanode. An electric potential can then be placed across the coating to direct the flow of electrons to a porous carbon counter-electrode that

has a high surface area and would collect any heavy metal ions present in the liquid. In addition, an applied electric potential can improve the destruction efficiency of organic contaminants by reducing electron-hole recombination on the catalyst surface. This recombination is seen as a primary reason for the observed inefficiency of other UV/ $\text{TiO}_2$  systems when treating organics in groundwater. Lastly, the electric potential has been shown to reduce the interference of electrolytes on the oxidation process. Electrolytes such as the bicarbonate ion are known hydroxyl radical scavengers and can be problematic in the UV/ $\text{TiO}_2$  treatment of contaminated groundwater.

This technology improves on liquid-phase photocatalytic technologies by distributing radiation uniformly throughout the reactor. Also, the technology does not require additional oxidants, such as peroxide or ozone, to cause complete mineralization or to improve reaction rates. In



Photoreactor Design using Ceramic Film

addition, it eliminates the need for an additional unit to separate and recover the catalyst from the purified water after the reaction is complete.

### **WASTE APPLICABILITY:**

This particular technology is designed to treat groundwater and dilute aqueous waste streams contaminated with organics and heavy metals. Organics are completely oxidized to carbon dioxide, water, and halide ions. Heavy metals are subsequently stripped from the cathode and recovered.

### **STATUS:**

The UW-Madison photocatalytic technology was accepted into the SITE Emerging Technology Program in 1995. The overall objective of the Emerging Technology Program study is to refine the reactor design, enabling it to treat heavy metals as well as organic contaminants. Testing of a bench-scale unit is currently underway.

UW-Madison has tested its photocatalytic reactor at the laboratory scale on aqueous solutions of several organic contaminants, including polychlorinated biphenyls, chlorosalicylic acid, salicylic acid, and ethylenediamine tetraacetate. UW-Madison has also used similar reactors to remove volatile organic compounds, such as trichloroethene, tetrachloroethene, benzene, and ethylene from air streams. Photooxidation of trichloroethene and tetrachloroethene has been successfully field-tested at low flow rates (<0.1 standard cubic feet per minute).

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